

Exhibit 6



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 762 930 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
12.07.2000 Bulletin 2000/28

(51) Int Cl.: B01J 20/04, C10G 11/04,
B01J 20/06

(21) Application number: 95920543.6

(86) International application number:
PCT/US95/06323

(22) Date of filing: 19.05.1995

(87) International publication number:
WO 95/32797 (07.12.1995 Gazette 1995/52)

(54) ABSORBENT AND PROCESS FOR REMOVING SULFUR OXIDES FROM A GASEOUS MIXTURE

SORBENTMITTEL UND VERFAHREN ZUR ENTFERNUNG VON SCHWEFETOXYDEN AUS EINER
GASMISCHUNG

ABSORBANT ET PROCEDE D'EXTRACTION D'OXYDES DE SOUFRE D'UN MELANGE GAZEUX

(84) Designated Contracting States:
DE NL

- FORAL, Michael, J.
Aurora, IL 60504 (US)
- REAGAN, William, J.
Naperville, IL 60540 (US)

(30) Priority: 01.06.1994 US 252175

(74) Representative: Ritter, Stephen David et al
Mathys & Squire
100 Grays Inn Road
London WC1X 8AL (GB)

(43) Date of publication of application:
19.03.1997 Bulletin 1997/12

(56) References cited:

(73) Proprietor: BP Amoco Corporation
Chicago, IL 60601 (US)

EP-A- 0 318 099	WO-A-87/06156
WO-A-91/10505	US-A- 4 774 212
US-A- 5 246 899	US-A- 5 288 675
US-A- 5 426 083	

(72) Inventors:

- BHATTACHARYYA, Alakananda
Wheaton, IL 60187 (US)

EP 0 762 930 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**BACKGROUND OF THE INVENTION****5 I. Field of the Invention**

[0001] The invention relates to anionic, hydrotalcite-type pillared clay compositions and their heat-treated derivatives. The invention also relates to a process for reducing the sulfur oxide content of a gaseous mixture by absorbing sulfur oxides on an absorbent which can be reactivated for further absorption through contact with a hydrocarbon in the presence of a hydrocarbon cracking catalyst.

10 II. Description of the Prior Art

[0002] The development of efficient methods and catalysts for reducing the concentration of air pollutants, such as sulfur oxides, in gaseous mixtures which result from the processing and combustion of sulfur-containing fuels presents a major industrial problem which has interested researchers for a considerable time. For example, U.S. Patent No. 3,835,031, issued to Bertolacini et al. and assigned to the assignee of the present application, describes a cyclic, fluidized catalytic cracking process operating with a catalyst comprising a molecular sieve in a silica-alumina matrix which is impregnated with one or more Group IIA metal oxides, such as magnesium oxide. By absorbing sulfur oxide within a regeneration zone and, subsequently, releasing the absorbed sulfur within a cracking reaction zone, emission of sulfur oxides in a regenerator stack gas stream is greatly reduced.

[0003] Other researchers have noted that absorbents containing rare earth metals are suitable for sulfur oxide removal service. U.S. Patent No. 4,146,463, issued to Radford et al. and assigned to the assignee of the present invention, describes the absorption of sulfur oxides by modified catalyst particles containing the oxides of rare earth metals, such as cerium, lanthanum and neodymium. The modified catalyst particles reportedly form non-volatile sulfur compounds by reacting with sulfur oxides in a regeneration zone.

[0004] Researchers have attempted to identify an optimal structure for sulfur oxides separation catalysts. U.S. Patent No. 4,626,419, issued to Lewis et al., is directed to a composition of matter for removing sulfur oxides from gases which comprises an alkali metal and a crystalline rare earth oxide, such as cerium oxide, having a crystal size of less than about 90 Angstrom units. The '419 Patent states that improved results measured as a reduction of sulfur in regenerator off-gas may be obtained using oxide crystals in the specified size range.

[0005] Sulfur oxide separation catalysts containing magnesium and aluminum crystalline structures in spinel form are reported, for example, in U.S. Patent No. 4,790,982, issued to Yoo et al., which describes the use of a magnesium and aluminum spinel in conjunction with cerium metal and free magnesia. U.S. Patent No. 4,728,635, issued to Bhattacharyya et al., is directed to a process for the production of a calcined alkaline earth, aluminum-containing spinel composition for use as a sulfur oxide and nitrogen removal agent.

[0006] U.S. Patent No. 4,865,019, issued to Van Broekhoven, describes sulfur-oxide absorbents which comprise an anionic clay having a hydrotalcite structure. The '019 Patent states that the anionic clay can have a layered structure corresponding to a formula calling for divalent cations, trivalent cations, and anions in specified proportions. Preference is given to divalent cations Mg^{2+} and trivalent cation Al^{3+} alone or combined with La^{3+} and/or Ce^{3+} . Anions NO_3^- , OH^- , Cl^- , Br^- , I^- , CO_3^{2-} , SO_4^{2-} , SiO_3^{2-} , SiO_2^{2-} , CrO_4^{2-} , HPO_4^{2-} , MnO_4^- , $HGaO_3^{2-}$, HVO_4^{2-} , ClO_4^{2-} , BO_3^{2-} , monocarboxylates, dicarboxylates, alkyl sulfonates, and combinations thereof are listed as suitable. The '019 Patent states that the absorbents are useful after a heat treatment to a temperature in the range of about 300 to about 900°C which reportedly can involve some decomposition of the hydrotalcite structure.

[0007] U.S. Patent No. 4,774,212, issued to Drezdon and assigned to the assignee of the present invention, describes magnesium and aluminum hydrotalcite-type clay compositions having polyoxometalates of vanadium, tungsten, or molybdenum as pillaring anions. The compositions are reported to have an x-ray diffraction $d(003)$ value which is larger than that of typical hydrotalcites, indicating a greater spacing between clay layers. Reference is made to use of the compositions for catalysis at temperatures in the range of about 200 to about 600°C. The '212 Patent also presents a method of preparing the described compositions which involves formulating hydrotalcite-like clays pillared by relatively large organic anions and replacing the organic anions with polyoxometalates from a solution having a pH of about 3 to about 6.

[0008] A direct and relatively simplified process for making anionic clays having a hydrotalcite structure pillared by pH-dependent inorganic anions is set forth in U.S. Patent No. 5,246,899, issued to Bhattacharyya and assigned to the assignee of the present invention. In a preferred aspect, the process comprises adding a solution containing one or more selected divalent cations and one or more selected trivalent cations to an essentially carbonate-free solution which includes an inorganic ion and has a selectively chosen pH between about 6 and 14.

[0009] U.S. Patent No. 5,288,675, issued to Kim, contemplates a $MgO/La_2O_3/Al_2O_3$ ternary oxide base wherein the

MgO component is present as a microcrystalline phase which may be detected by x-ray diffraction. The ternary oxide base can reportedly be used in combination with ingredients such as ceria and/or vanadia to control sulfur oxide emissions. The '675 Patent states that the combination can be prepared by a multi-step process which includes reacting an aged, coprecipitated lanthanum and aluminum hydroxide slurry with a magnesium oxide slurry and a sodium hydroxide solution, calcining, impregnating with solutions of cerium and/or vanadium and calcining at a temperature of 450° to 700°C.

[0010] Sulfur oxide emissions from fluid catalytic cracking units, for example, are increasingly restricted by environmental regulations. The removal of sulfur oxide pollutants has been the subject of considerable attention for several years. One approach to reducing such emissions involves desulfurizing a hydrocarbon feed stream before it enters the cracking unit, so that a lesser amount of sulfur oxides are produced. Another approach is to scrub the emissions stream with an inexpensive alkaline material, such as lime or limestone. However, both of these approaches are relatively cumbersome and they create other waste disposal problems. Accordingly, separating the sulfur oxides by contact with a reusable absorbent presents an appealing alternative.

[0011] It is generally accepted that sulfur trioxide (SO₃) absorption proceeds more rapidly than sulfur dioxide (SO₂) absorption. Accordingly, efficient sulfur dioxide absorbents must perform at least three functions. First, desirable absorbents have a catalytic capability that allows them to enhance the reaction of sulfur dioxide with oxygen to form sulfur trioxide. Second, desirable absorbents are capable of binding sulfur trioxide in relatively large amounts. Third, desirable absorbents can desorb sulfur components comparatively quickly on exposure to hydrocarbons and cracking catalyst.

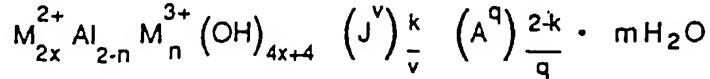
[0012] The sulfur oxide absorbents which have received the widest commercial acceptance to date in fluidized catalytic cracking units are based on spinel technology, most notably MgAl₂O₄ spinels combined with cerium oxide. Although the spinel and cerium absorbents are adequate for many purposes, they exhibit limited absorbent capacity and are prone to deactivation. In particular, free cerium oxide crystals present in the spinel and cerium absorbents tend to increase in size during normal operation so as to inhibit overall activity. Additionally, the spinel and cerium absorbents require more time for complete desorption than is available in some cyclic processing schemes.

[0013] Accordingly, a need still exists for new absorbents which can absorb and desorb comparatively larger amounts of sulfur compounds per unit mass within relatively short cycle time periods. Catalytic materials on the absorbents must be well dispersed for maximum accessibility and resist the tendency to agglomerate under operating conditions. Additionally, the absorbents should resist physical attrition and demonstrate superior stability at processing temperatures in both oxidizing and reducing environments.

SUMMARY OF THE INVENTION

[0014] The invention is an improved absorbent composition composed substantially of relatively small microcrystallites which demonstrate desirable sulfur oxide absorption capacity and comparatively fast absorption and desorption rates. High resolution electron microscopy reveals that a substantial portion of the microcrystallites are essentially composed of a solid solution having impurities, such as aluminum oxide, dispersed in a monoxide of a divalent metal. The improved absorbent also includes spinel microcrystallites and trivalent metal oxide microcrystallites. The improved absorbent can be produced by heat treating layered mixed hydroxide compositions having interlayer anions in monometalate, dimetalate, trimetalate, or tetrametalate form. The invention is also a sulfur oxide separation process which exploits the advantages of the improved absorbent.

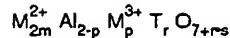
[0015] In a preferred aspect, the invention is an anionic layered mixed hydroxide composition having the formula:



where M²⁺ is a divalent metal selected from the group consisting of magnesium, calcium, zinc, barium, and strontium. M³⁺ is a trivalent metal cation selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium, and cobalt.

[0016] J is VO₃, HVO₄, VO₄, V₂O₇, HV₂O₇, V₃O₉, V₄O₁₂, WO₄ or MoO₄. A is selected from the group consisting of CO₃, OH, SO₃, SO₄, Cl, and NO₃. q and v are the net ionic charges associated with J and A, respectively. x is 1.1 to 3.5, while n is 0.01 to 0.4, m is a positive number.

[0017] In another preferred aspect, the invention is a composition suitable for use as a sulfur oxide absorbent. The absorbent comprises microcrystallites collectively of the formula:



5 where M^{2+} is a divalent metal, and M^{3+} is a trivalent metal, as described above. T is vanadium, tungsten or molybdenum, with the proviso that T and M^{3+} cannot both be vanadium p is 0.01 to 0.4, while r is 0.01 to 0.2. s is 2.5 when T is vanadium or 3 when T is tungsten or molybdenum. Each of the microcrystallites has a greatest linear dimension in the range of 0.1 to 30 nanometers. Moreover, a substantial portion of the microcrystallites of the invention are essentially composed of a solid solution phase having impurities, such as aluminum oxide or vanadium oxide, dispersed in a monoxide of the divalent metal. Another portion of microcrystallites are essentially composed of a spinel phase.

10 [0018] In yet another preferred aspect, the invention is a process for manufacturing a composition suitable for use as a sulfur oxide absorbent. In the process, water is blended with about two molar parts of a salt of a divalent metal selected from the group consisting of magnesium, calcium, zinc, strontium, and barium. Additionally, one molar part in sum of an aluminum salt and a selected trivalent metal is also blended in the mixture. The trivalent metal is selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium and cobalt. A metolate salt in a quantity of 0.1 to less than 2 molar parts is also blended into the mixture. The metolate salt contains an anionic species which is a vanadate, a tungstenate, or a molybdenate. In an especially preferred aspect, an alkalinity control agent is also blended into the mixture to stabilize the anion in an aqueous, dissociated form which contains but a single metal atom. Anions in such form are commonly described as monometolate. It is sometimes convenient to introduce the anions in solution form as a separate step after a precipitate has formed and has been calcined at least once.

15 [0019] The mixture is heated to a temperature in the range of 50° to 100°C for at least one hour and, thereafter, an anionic layered mixed hydroxide is recovered from the mixture. The recovered layered hydroxide is calcined for about one hour at a temperature of 450°C or hotter to produce a collapsed composition suitable for use as a sulfur oxide absorbent. The collapsed composition is substantially composed of microcrystallites having a greatest linear dimension in the range of 0.1 to 30 nanometers. The collapsed composition contains microcrystallites which are essentially composed of a solid solution phase having aluminum oxide or vanadium oxide dispersed in a monoxide of the divalent metal. The collapsed composition also contains microcrystallites which are essentially composed of a spinel phase.

20 [0020] In an additionally preferred aspect, the invention is a process for manufacturing a composition suitable for use as a sulfur oxide absorbent which comprises calcining a layered mixed hydroxide at a temperature of at least 450°C for one hour or more. The layered hydroxide is of the formula set forth above in regard to layered mixed hydroxides of the invention. The product of calcining is a collapsed composition substantially composed of microcrystallites, each of 0.1 to 30 nanometers in size. The microcrystallites are constituted by solid solution phase microcrystallites and by spinel phase microcrystallites, as described above.

25 [0021] Moreover, the invention is a process for separating sulfur oxides from gaseous mixtures. The process comprises absorbing sulfur oxides on a dehydrated and collapsed composition which is substantially composed of microcrystallites collectively of the formula set forth above with regard to collapsed compositions of the invention. The microcrystallites are of 0.1 to 30 nanometers. One portion of the microcrystallites is constituted by a solid solution phase and another portion of the microcrystallites is constituted by a spinel phase, as described above. The process additionally comprises desorbing sulfur dioxide from the absorbent by contacting the collapsed composition with a hydrocarbon in the presence of a cracking catalyst.

30 [0022] The invention is also a process for the cyclic fluidized catalytic cracking of a hydrocarbon feedstock containing organic sulfur compounds. The process comprises absorbing at least a portion of the sulfur oxides in a regeneration zone with a fluidizable particulate solid including a collapsed composition in accordance with the formula set forth above. The collapsed composition includes microcrystallites composed essentially of a solid solution phase having aluminum oxide dispersed in a monoxide of a divalent metal, as described above. The process further includes removing absorbed sulfur oxides from the particulate solid by exposing the particulate solid to the hydrocarbon feedstocks in the reaction zone.

BRIEF DESCRIPTION OF THE DRAWINGS

50 [0023]

FIG. 1 is the trace of an x-ray diffraction analysis for the product of Example 1, showing a relationship between intensity and an angle (in degrees) that is characteristic of a mixed layered hydroxide structure having a $d(001)$ value of 7.62 Angstroms units;

55 FIG. 2 is a dual-axis graph showing a relative weight for the product of Example 2 as a function of time (in minutes) during the course of a thermal gravimetric analysis having a temperature trace which is also presented in FIG. 2; FIG. 3 is a dual-axis graph which depicts a relative weight for the product of Example 3 as a function of time during the course of a thermal gravimetric analysis having a temperature trace which is also presented in FIG. 3; and

FIG. 4 is a dual-axis graph exhibiting a relative weight trace and a temperature trace for a second cycle and a third cycle of thermal gravimetric analysis performed on the product of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

5

[0024] We have discovered that anionic layered mixed hydroxide compositions can be calcined to produce dehydrated and collapsed compositions having unique solid solution microcrystallites that are very suitable for use as sulfur oxide absorbents. The layered compositions will be described first.

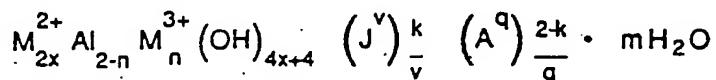
10

[0025] Anionic layered mixed hydroxide compositions are layered in the sense that they are constituted by sheets of divalent and trivalent metal cations interposed between a larger number of hydroxide anions which are also in the sheets. They are mixed because divalent cations and trivalent cations are interspersed within the sheets. Water molecules and additional anions are located in interlayers between the sheets. When subjected to conventional x-ray diffraction analysis, the layered mixed hydroxide composition exhibits diffraction peaks whose positions can be correlated with the average distance between adjacent sheets.

15

[0026] In one aspect, the invention is an anionic layered mixed hydroxide composition of the formula:

20



25

[0027] In the formula, M^{2+} is a divalent metal present as a cation having a valence of positive two which is coordinated with a plurality of hydroxide anions to form infinite sheets. The structure of the sheets resembles the structure of the naturally occurring mineral brucite, $Mg(OH)_2$. The divalent metal is preferably selected from the elements of Group IIA or IIB of the periodic table of the elements as depicted on the inside front cover of Perry's Chemical Engineers Handbook (6th Edition). More preferably, the divalent metal is selected from the group consisting of magnesium, calcium, zinc, strontium, and barium; most preferably from the group consisting of magnesium, calcium, and zinc.

30

[0028] The symbol M^{3+} denotes a trivalent metal present as a cation of valence three. The trivalent metal is preferably selected from the group consisting of rare earth elements, iron, chromium, vanadium, and cobalt. More preferably, the trivalent metal is selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium, and cobalt; most preferably cerium and lanthanum. The rare earth elements, also known as the lanthanide series elements, are often found as a naturally occurring mixture of two or more of the rare earth elements. It is contemplated that such mixtures of rare earth elements may be conveniently employed in the present invention.

35

[0029] x is 1.1 to 3.5; preferably 1.5 to 3.5; and more preferably 2 to 3. n is 0.01 to 0.4, more preferably 0.2 to 0.4. Al is the trivalent metal aluminum present as a trivalent cation coordinated with a plurality of hydroxide anions. Additionally, it is preferred that the molar ratio of the divalent metal to aluminum be 1 to 5, more preferably 2 to 3.

40

[0030] J is an anion selected from the group consisting of vanadates, tungstenates and molybdates. Preferably, J is VO_3 , HVO_4 , VO_4 , V_2O_7 , HV_2O_7 , V_3O_9 , V_4O_{12} , WO_4 or MoO_4 . More preferably, J is selected from the group consisting of monovanadates, specifically metavanadate (VO_3), orthovanadate, (VO_4) and protonated vanadate (HVO_4). Preferably, J is located primarily in interlayers between the sheets, v is the net anionic charge associated with J . For example, the net ionic charge associated with VO_3^{1-} is -1. Similarly, the net ionic charge associated with HVO_4^{2-} is -2.

45

[0031] A is a relatively small anion having a size approximately equal to or less than that of carbonate (CO_3). Preferably, A is selected from a group consisting of CO_3 , OH , SO_3 , SO_4 , Cl , and NO_3 . q is the net ionic-charge associated with A . k is 0.01 to less than 2.

50

[0032] m is a positive number quantitatively indicating the presence of water molecules. Preferably, substantially all of the water molecules are located in the interlayer. However, the formula presented is empirical and is not limited to any particular structure.

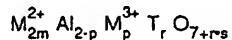
55

[0033] By way of comparison, the naturally occurring mineral hydrotalcite is a specific example of an anionic layered mixed hydroxide composition. However, the formula of hydrotalcite differs from the formula of the layered composition of the present invention in that the mineral hydrotalcite ordinarily contains substantially no divalent metals other than magnesium, substantially no trivalent metals other than aluminum, and substantially no anions other than carbonate.

[0034] The layered composition of the present invention exhibits an x-ray diffraction pattern when analyzed using conventional techniques, preferably an x-ray diffraction pattern including a $d(001)$ value equal to or greater than 7.6 Angstrom units. An especially preferred layered composition employs magnesium as the divalent metal, cerium as the trivalent metal, and a monovanadate as the anion J .

[0035] In another aspect, the invention is a dehydrated and at least partially collapsed composition suitable for use as a sulfur oxide removal catalyst. Preferably, the collapsed composition is prepared by heat treating the layered com-

position described above. Regardless of its source or method of preparation, the collapsed composition comprises microcrystallites which are collectively of the formula:



[0036] In the formula, M^{2+} is a divalent metal, Al is aluminum and M^{3+} is a trivalent metal, as described above. T is vanadium, tungsten or molybdenum, preferably vanadium with the proviso that T and M^{3+} cannot both be vanadium when M^{2+} is magnesium.

10 [0037] m is preferably 1.1 to 3.5, more preferably 1.5 to 3.5, and most preferably 2 to 3. p is 0.01 to .4, preferably 0.2 to 0.4. It is preferred that the molar ratio of the divalent metal to aluminum be 1 to 5, more preferably 2 to 3.

[0038] r is 0.01 to 0.2, preferably 0.05 to 0.2. In the algebraic expression communicating the subscript for O in the above formula, r is multiplied times s. s is 2.5 when T is vanadium, but s is 3 when T is tungsten or molybdenum.

15 [0039] Each of the microcrystallites of the invention has certain identifying characteristics. It is not necessary that every microcrystallite present in a composition possess these characteristics, but a substantial proportion of the microcrystallites must possess the characteristics in order to achieve the advantages offered by the invention.

[0040] First, the microcrystallites of the invention have a greatest linear dimension in the range of 0.1 to 30 nanometers, more preferably 1 to 20 nanometers and most preferably 10 nanometers. The microcrystallites need not be spherical. For microcrystallites which are spherical, the greatest linear dimensions are the diameters.

20 [0041] Absorbents having microcrystallites with dimensions in the specified range are sometimes termed "amorphous," possibly because conventional x-ray diffraction analysis techniques are inadequate to detect the presence of their relatively small crystal structure. However, high resolution electron microscopy routinely detects microcrystallites in this size range. For the present purposes, high resolution electron microscopy is defined as electron microscopy capable of a point-to-point resolution of at least 2.0 Angstrom units.

25 [0042] Such electron microscopy is also capable of detecting lattice planes in microcrystallites. A lattice plane is a regular geometrical arrangement of objects in space, such as atoms arranged in a crystalline structure, that is relatively flat in a given vicinity. When viewed on edge by appropriate electron microscopy techniques, the lattice planes appear as lines which can be curved or straight as well as continuous or discontinuous.

30 [0043] Additionally, the electron microscopy techniques can pinpoint the existence and location of individual lattice planes, the relative intensity of various lattice planes, and the spacing between adjacent lattice planes. Taken together, these observations of the crystal lattice, termed "lattice parameters," can be used to distinguish between two or more phases within a high resolution electron microscope's field of view. Herein, a phase is understood to be a homogeneous, physically distinct portion of matter present in a non-homogeneous physical-chemical system.

35 [0044] In practice, the lattice planes exhibit identifying lattice parameters, such as spacing, relative intensity, and periodic repetitions in spacing and intensity, which can be utilized to distinguish between phases. Once the presence of distinguishable phases has been determined, it may be necessary to carry out other types of analyses in order to precisely determine compositions of the phases. For example, scanning electron microscopy is often used to confirm the phase compositions.

40 [0045] Secondly, a substantial portion of the microcrystallites of the present invention are essentially composed of a solid solution phase in which an impurity, such as aluminum oxide (Al_2O_3) or vanadium oxide, is dispersed within a crystal lattice of a monoxide of a divalent metal, such as magnesium oxide (MgO). The dispersion is not merely a physical aggregation. Rather, the impurity is present as a dopant. The impurities are located so as to expand the crystal lattice of the divalent metal monoxide but not to disrupt the crystal lattice completely.

45 [0046] Another portion of the microcrystallites is composed essentially of a spinel phase. For example, the spinel phase may include a magnesium spinel such as $MgAl_2O_4$. Additionally, microcrystallites composed essentially of an oxide of the trivalent metal are preferably present.

50 [0047] The solution solid phase having aluminum oxide dispersed in a divalent monoxide crystalline structure is considered to be highly unusual. It is much more common to find relatively separate microcrystallites of aluminum oxide and the divalent monoxide together, with each microcrystallite containing but a single oxide. Accordingly, it is hypothesized that the presence of the solid solution phase of the present invention indicates a tendency to resist further division between the two phases. It is believed that the presence of the solid solution phase correlates with improved stability and activity under hydrocarbon processing conditions.

55 [0048] The divalent metal oxide phase can be selected from the Group IIA and Group IIB elements. Preferably the divalent metal is selected from the group consisting of magnesium, calcium, zinc, strontium, and barium, more preferably from the group consisting of magnesium, calcium and zinc. It is especially preferred that the divalent metal oxide phase be composed essentially of magnesium oxide.

[0049] The spinel phase is constituted by elements in crystalline spinel form, although the spinel may be present as microcrystallites too small to be detected by conventional x-ray diffraction analyses. The spinel structure is based on

a cubic close packed array of oxide ions. Typically, the crystalline unit cell of the spinel structure contains 32 oxygen atoms. With regard to magnesium aluminum oxide spinel, there are 8 magnesium atoms and 16 aluminum atoms in each unit cell, corresponding to the formula $MgAl_2O_4$.

5 [0050] If oxide crystals of the trivalent metal described above are present, such as crystals of cerium oxide or lanthanum oxide, the trivalent metal oxide crystals each must be substantially in the form of microcrystallites having a greatest linear dimension in the range of 0.1 to 30 nanometers, preferably 1 to 20 nanometers. It is especially preferred that the trivalent metal be predominantly situated in relatively homogeneous microcrystallites of the present invention coexisting with solid solution microcrystallites and spinel microcrystallites.

10 [0051] It is hypothesized that the presence of the trivalent metal oxide phase with the other microcrystallites of the present invention provides a desirable degree of dispersion for the trivalent metal atoms and also tends to protect trivalent metal oxides from attrition. Cerium oxide crystals standing alone, for example, have a tendency to disintegrate under the stresses of fluidized bed processing.

15 [0052] In another aspect, the invention is a process for manufacturing a composition suitable for use as a sulfur dioxide absorbent. A mixture is produced by blending water with about two parts by moles of a salt of a divalent metal selected from the group consisting of magnesium, calcium, zinc, strontium, and barium; preferably magnesium. Additionally, about one part by moles of the combined sum of an aluminum salt and a salt of a trivalent metal selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium and cobalt is blended into the mixture. The sum is calculated by adding the molar amount of the aluminum salt to the molar amount of the trivalent metal salt and dividing the total by one-half of the molar amount of the divalent metal salt. Also blended in the mixture is 0.01 to less than 2 molar parts of a metalate salt. The metalate salt of the present invention contains an anion which is a vanadate, a tungstenate or a molybdate. Herein, salt is intended to mean a cation and an anion joined in an ionic bond. For convenience, we refer to solutions containing dissolved salts as salt solutions even though the ionic bonds have become dissociated.

20 [0053] In a preferred aspect, the process also includes blending into the mixture an appropriate amount of an alkalinity control agent to stabilize the anions in an aqueous, disassociated metalate form selected from the group consisting of monometalate, dimetalate, trimetalate, and tetrametalate anions. In an especially preferred aspect, the anions are monometalates which each contain exactly one metal atom. For example, VO_3^{1-} , HVO_4^{2-} , and VO_4^{3-} represent anions which each contain exactly one metal atom. Allowance must often be made for losses of the alkalinity agent to precipitation. Stabilization of the metalate anion typically takes place in a liquid phase portion of the blended mixture.

25 [0054] For the present purposes, blending is understood to include methods wherein all of the described ingredients are blended simultaneously, and also to include methods wherein two or more of the ingredients are blended with each other and then blended with other ingredients. At each successive combination of ingredients, care must be taken to provide concentrations and alkalinitiess which tend to precipitate desired divalent metals and trivalent metals, as described above. The alkalinity of the mixture can also determine which forms of the anions are stabilized in solution and ultimately become components of the precipitates. It is often convenient to delay addition of the metalate anions until after a precipitate has formed and has been subjected to recovery and calcining.

30 [0055] The final choice of blending amounts and conditions is guided by the knowledge of previous practitioners in the art. For example, U.S. Patent No. 5,246,899 and allowed U.S. patent application Serial No. 08/093,768, which are herein incorporated in their entirety, contain useful teaching regarding pH-dependent anions and intercalating agents. Additionally, pages 181 through 182 of "The Early Transition Metals," by D.L. Kepert, Academic Press (New York) are recommended for information on stabilizing vanadate ions in solution.

35 [0056] In an especially preferred aspect of the process, the metalate salt contains a vanadate and is blended in an amount sufficient to produce a concentration of the vanadate in a liquid phase of the mixture which is in the range of 0.01 to 1 molar. Additionally, sufficient alkalinity control agent resides in the liquid phase of the mixture to produce an alkalinity in the range of 6 to 14 pH. The range of 6 to 8 pH is appropriate for VO_3^{1-} . The range of 9 to 13 pH is appropriate for HVO_4^{2-} . The range of 13 to 14 is appropriate for VO_4^{3-} .

40 [0057] In this especially preferred aspect of the process, it is contemplated that 50 percent or more of the vanadate ions dissolved in the liquid portion of the mixture are in a monometalate vanadate form, such as HVO_4^{2-} , VO_4^{3-} or VO_3^{1-} . Because the metavanadate anion (VO_3^{1-}) and the orthovanadate anion (VO_4^{3-}) are stabilized at conditions which are inconsistent with the precipitation of many divalent metal hydroxides and trivalent metal hydroxides, it is often convenient to blend solutions containing these anions with the product of the recovery and the first calcination described above. Preferably, the product is calcined again after being exposed to the metalate salt solution.

45 [0058] The heated mixture is permitted to stand for at least 1 hour, preferably at a temperature in the range of 50° to 100°C, more preferably 75° to 100°C. Higher temperatures may be utilized provided that commensurately higher pressures exist to maintain at least a portion of the mixture in the liquid phase. An anionic layered mixed hydroxide, as described above, is recovered as a solid from the mixture. Appropriate recovery techniques include but are not limited to filtration, evaporation, fractional crystallization and spray drying.

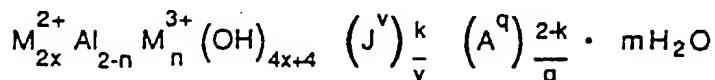
50 [0059] The recovered layered mixed hydroxide is calcined for not less than 1 hour at a temperature of 450°C or

hotter. Preferably the temperature is in the range of 450° to 1000°, more preferably 450° to 850°C. Herein, calcining refers to the heating of a solid in the presence of a gas, preferably a flowing gas. The gas may be air or, alternatively, a relatively inert gas, such as nitrogen, helium, or carbon dioxide. The recovered material may be calcined more than once; preferably before and after one or more exposures to a metalate salt solution as described above. The final calcining produces a dehydrated and collapsed composition suitable for use as a sulfur oxide absorbent.

5 [0060] The collapsed composition is dehydrated in the sense that it contains essentially no associated water molecules. Additionally, the sheets containing metal cations coordinated with hydroxide anions, as described above, are at least partially disrupted by the calcining and are in a condition conveniently termed "collapsed." Rather than having sheets of 400 nanometers or more in length as are typical of the layered mixed hydroxides, the collapsed composition 10 is substantially composed of microcrystallites, each having a greatest linear dimension in the range of 0.1 to 30 nanometers. It is hypothesized that the microcrystallites are disintegrated and jumbled remnants of the layered mixed hydroxides which are believed to have at least partially collapsed when subjected to the calcining. Repeated calcination steps interspersed by contact with aqueous solutions are believed to repeatedly disrupt and reform the layered sheets so as to produce a final collapsed product having an excellent degree of microcrystallite dispersion.

15 [0061] In any event, the microcrystallites of the invention are relatively small and well dispersed so as to be accessible to reactants such as sulfur oxides. A substantial portion of the microcrystallites are constituted by a solid solution phase having aluminum oxide dispersed in a divalent metal monoxide. Another portion is constituted by a spinel phase. The phases contain lattice planes discernible by high resolution electron microscopy.

20 [0062] In yet another aspect the invention is a process for manufacturing a composition suitable for use as a sulfur oxide absorbent which comprises calcining a layered mixed hydroxide of the formula:



25

[0063] M²⁺ is a divalent metal selected from the group consisting of magnesium, calcium, zinc, barium, and strontium. Divalent metals selected from the group consisting of magnesium, calcium, and zinc are preferable because in practice 30 they more readily form sheets of metal cations coordinated with hydroxide anions, as described above. Magnesium is especially preferred as the divalent metal.

[0064] x is 1.1 to 3.5, preferably 1.5 to 3.5; n is 0.01 to 0.4, preferably 0.1 to 0.3. The trivalent metal, M³⁺, is selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium and cobalt, preferably the trivalent metal is cerium, lanthanum or iron.

35 [0065] J is a monomeric anion selected from the group consisting of VO₃, HVO₄, VO₄, V₂O₇, HV₂O₇, V₃O₉, V₄O₁₂, WO₄, and MoO₄; v is the net ionic charge associated with J; and k is 0.01 to less than 2.

[0066] A is CO₃, OH, SO₃, SO₄, Cl, or NO₃; q is the net ionic charge associated with A; and m is a positive number.

[0067] The calcining is performed for one hour or more at a temperature of at least 450°C, preferably a temperature 40 in the range of 450° to 1000°, and more preferably a temperature in the range of 450° to 850°C. The calcining may be performed repeatedly, in two or more operations preferably interspersed by contacting with an aqueous metalate salt solution. The final calcining produces a dehydrated and collapsed composition, as described above.

[0068] In still another aspect, the invention is a process for separating sulfur oxides from a gas containing sulfur oxides which comprises absorbing sulfur oxides by exposing a gaseous mixture containing sulfur oxides to a dehydrated and collapsed composition, as described above. Herein the term "absorbing" is understood to include absorption, 45 adsorption, imbibition, and chemisorption. The sulfur oxides include sulfur dioxide and sulfur trioxide. The absorbing causes the sulfur oxide to become associated with and remain in close proximity to the collapsed composition. It is not entirely clear whether the sulfur oxides are associated in the form of sulfur trioxide molecules, an anion containing sulfur and oxide, or some other chemical species.

[0069] The gaseous mixture from which sulfur oxides are removed need not contain molecular oxygen, but in a 50 preferred aspect of the invention desirably contains an amount of molecular oxygen which is in excess of the stoichiometric amount required to convert any sulfur dioxide present to sulfur trioxide. The excess of molecular oxygen need not be large, but the ability of the absorbent of this invention to absorb sulfur dioxide is improved as the amount of excess molecular oxygen increases. Although the reason for this effect by molecular oxygen is uncertain, it is believed that increased concentrations of oxygen promote the conversion of sulfur dioxide to sulfur trioxide and assist in rejuvenating an oxidation function of the adsorbent. It is also believed that this sulfur trioxide is more easily absorbed by the absorbent than is the sulfur dioxide. The molecular oxygen can either be inherently present in the sulfur oxide containing gaseous mixture or can be added. The absorption of sulfur oxides is desirably carried out at a temperature below 900°C, preferably at a temperature of 100° to 900°C and most preferably at a temperature of 300° to 800°C.

[0070] The sulfur oxides are desorbed by contacting the collapsed composition with a hydrocarbon in the presence of a cracking catalyst at an elevated temperature. The temperature is desirably 375° to 900°C, preferably 430° to 700°C, and most preferably 450° to 650°C. Any hydrocarbon can be used to remove the absorbed sulfur oxides from the absorbent of this invention so long as it can be cracked by the cracking catalyst at the temperatures employed.

5 Suitable hydrocarbons include, but are not limited to methane, natural gas, natural gas liquids, naphtha, light gas oils, heavy gas oils, wide-cut gas oils, vacuum gas oils, decanted oils, and reduced crude oils as well as hydrocarbon fractions derived from shale oils, coal liquefaction and the like; such hydrocarbons can be employed either singly or in any desired combination. Additionally, the sulfur oxides can be desorbed by contact with a reducing gas such as hydrogen.

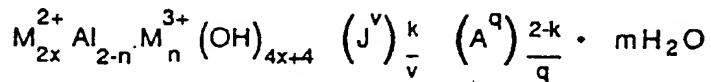
10 [0071] Although the invention disclosed herein is not to be so limited, it is hypothesized that a chemical reaction occurs between the collapsed composition and the sulfur oxides which results in the formation of non-volatile inorganic sulfur compounds, such as sulfites and sulfates, at relatively high temperatures. These sulfites and sulfates can undergo partial decomposition to liberate the original sulfur oxides and collapsed composition. As a consequence of this reversal of the sulfur oxide absorption at high temperature, the absorption of sulfur oxides is desirably effected at a temperature below 900°C and preferably below 800°C.

15 [0072] The precise mechanism by which absorbed sulfur oxides are removed from the collapsed composition is unknown, but it is believed that the combination of hydrocarbons and hydrocarbon cracking catalyst and elevated temperatures produces a reducing environment which effects a conversion of absorbed sulfur oxides to hydrogen sulfide while simultaneously reactivating the collapsed composition for further absorption of sulfur oxides. The removal of absorbed sulfur oxides from the collapsed composition is generally improved by contacting the collapsed composition with added steam either simultaneously with or subsequent to treatment with a hydrocarbon in the presence of a cracking catalyst.

20 [0073] The hydrogen sulfide which is produced during the removal of absorbed sulfur oxides from the collapsed composition can be converted to elemental sulfur by any of the conventional techniques which are well-known to the art as, for example, in a Claus Unit. Cracked hydrocarbon products which are produced during removal of absorbed sulfur oxides can be recycled for further use in removing absorbed sulfur oxides.

25 [0074] It is highly preferable that the process for separating sulfur oxides further comprise exposing a layered mixed hydroxide of the formula:

30



35

where M^{2+} is a divalent metal selected from the group consisting of magnesium, calcium, and zinc;

x is 1.1 to 3.5;

n is 0.01 to 0.4;

40 M^{3+} is a trivalent metal selected from the group consisting of cerium, iron, chromium, vanadium and cobalt;

J is VO_3 , HVO_4 , V_2O_7 , HV_2O_7 , V_3O_9 , V_4O_{12} , VO_4 , WO_4 or MoO_4 ;

v is the net ionic charge associated with J;

k is 0.01 to less than 2;

A is selected from the group consisting of CO_3 , OH , SO_3 , SO_4 , Cl , NO_3 ;

q is the net ionic charge associated with A; and

45 m is a positive number,

to the gaseous mixture containing sulfur oxides at a temperature in the range of 450° to 1000°C to produce the collapsed composition described above.

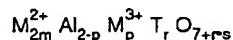
50 [0075] Suitable cracking catalyst for use in the practice of this invention includes all high activity solid catalysts which are stable under the required conditions. Suitable catalysts include those of the amorphous silica-alumina type, having an alumina content of 10 to 30 weight percent. Catalysts of the silica magnesia type are also suitable which have a magnesia content of 20 weight percent. Preferred catalysts include those of the zeolite-type which comprise from 0.5 to 50 weight percent and preferably 1 to 30 weight percent of a crystalline alumina silicate compound distributed through a porous matrix. Zeolite-type cracking catalysts are preferred because of their thermal stability and high catalytic activity.

55 [0076] The crystalline alumina silicate or zeolite component of the zeolite-type cracking catalyst can be of any type or combination of types, natural or synthetic, which is known to be useful in catalyzing the cracking of hydrocarbons. Suitable zeolites include both naturally occurring and synthetic alumina silicate materials such as faujasite, chabazite, mordenite, Zeolite X, Zeolite Y, and ultra-stable large pore zeolites. The zeolite-type cracking catalyst may be dispersed

within a porous refractory material, natural or synthetic, which can be, for example, silica, alumina magnesia, boria, kieselguhr, diatomaceous earth, and mullite.

5 [0077] In the practice of this invention, the collapsed composition can be incorporated into or deposited onto a suitable support. Suitable supports include, but are not limited to, amorphous cracking catalyst, zeolite-type cracking catalyst, silica, alumina, mixtures of silica and alumina, magnesia, mixtures of silica and magnesia, kieselguhr, kaolin, and diatomaceous earth. Preferably the support is porous and has a surface area including the area of the pores open to the surface of at least 10, preferably at least 50, and most preferably 100 square meters per gram.

10 [0078] A highly preferred aspect of this invention comprises its use to reduce sulfur oxide emissions from catalyst regeneration in a cyclic, fluidized, catalytic cracking process. In this embodiment, a fluidizable particulate solid which comprises a dehydrated and collapsed composition is circulated through the fluidized catalytic cracking process in association with a particulate cracking catalyst. The collapsed composition is of the formula:



15 [0079] The collapsed composition is substantially composed of microcrystallites of 0.1 to 30 nanometers. One portion of the microcrystallites are constituted by a solid solution phase having alumina oxide dispersed in a divalent metal monoxide crystal structure. Another portion of the microcrystallites is constituted by a spinel phase. Additionally, microcrystallites constituted by a trivalent metal oxide phase may be present. The phases are discernible by high resolution electron microscopy.

20 [0080] A feedstock is mixed with a particulate cracking catalyst in a reaction zone at a temperature in the range of 430°C to 730°C to produce cracked hydrocarbons. The contact with the cracking catalyst is preferably effected in one or more fluidized transfer line reactors at cracking temperature and at a fluidizing velocity which limits the cracking time to not more than 10 seconds. Reaction zone effluent, comprises hydrocarbon vapors both cracked and uncracked, 25 cracking catalyst and a carbonaceous material referred to as coke which contains sulfur, relatively volatile carbonaceous components and relatively less volatile carbonaceous components. A significant proportion of the coke adheres to the cracking catalyst.

30 [0081] The carbonaceous components of coke comprise highly condensed aromatic hydrocarbons which generally contain a minor amount of hydrogen, generally from 4 to 10 weight percent of hydrogen. When the hydrocarbon feedstock contains organic sulfur compounds, the coke also contains sulfur. As the coke builds up on the cracking catalyst, the activity of the catalyst for cracking and the selectivity of the cracking catalyst diminishes. The catalyst can, however, recover a major portion of its original capabilities by a suitable regeneration process.

35 [0082] Hydrocarbon vapors are separated from the cracking catalyst, and the cracking catalyst is stripped of volatile deposits before regeneration. The stripping zone can be suitably maintained at a temperature in the range of 430°C to 700°C, preferably 450° to 650°C and most preferably from 765° to 595°C. The preferred stripping gas is steam although inert gases, such as nitrogen or flue gases, or mixtures of steam with inert gases can also be used.

40 [0083] Stripped and partially deactivated cracking catalyst is regenerated by burning the coke deposits from the catalyst surface with a molecular oxygen containing regeneration gas, such as air, in a regeneration zone. This burning results in the formation of combustion products such as sulfur oxides, carbon monoxide, carbon dioxide and steam.

45 [0084] The oxygen containing regeneration gas can contain relatively inert gases such as nitrogen, steam, carbon dioxide, recycled regeneration zone effluent and the like. The molecular oxygen concentration of the regeneration gas is ordinarily from 2 to 30 volume percent and preferably from 5 to 25 volume percent. Since air is conveniently employed as a source of molecular oxygen, a major portion of the inert gas can be nitrogen. The regeneration zone temperatures are ordinarily in the range of 565° to 790°, and are preferably in the range of 620° to 735°.

50 [0085] During the catalytic cracking of the hydrocarbon feedstock in the reaction zone absorbed sulfur oxides are substantially released from the particulate solid as sulfur containing gas comprising hydrogen sulfide. Similarly, subsequent steam stripping serves not only to remove the volatile coke components from the cracking catalyst, but also serves to complete the removal of any residual absorbed sulfur oxides from the particulate solid and complete the reactivation of the collapsed composition for further absorption of sulfur oxides in the regeneration zone. The resulting hydrogen sulfide is recovered together with other products from the reaction zone, and stripping zones and can be converted to elemental sulfur in facilities which are conventionally associated with a fluidized catalytic cracking unit.

55 [0086] The following Examples are not intended to limit the scope of the invention in any manner but, rather, are presented in order to better communicate certain aspects of the invention.

Example 1: Preparation of a Layered Mixed Hydroxide

[0087] One liter of deionized water, 15.90 grams (0.15 mol) of sodium carbonate, and 48.0 grams (1.2 mol) of sodium hydroxide were charged to a flask equipped with a mechanical stirrer and a water-cooled reflux condenser. One liter of deionized water, 102.56 grams (0.4 mol) of $Mg(NO_3)_2 \cdot 6H_2O$, 67.38 grams (0.1796 mol) of $Al(NO_3)_3 \cdot 9H_2O$, and 8.86 grams (0.0204) of $Ce(NO_3)_3 \cdot 6H_2O$ were blended and added dropwise to the flask with continuous stirring over a period of about one hour. The result was a gelatinous mixture of 10.74 pH which was heated under reflux while being swept with a nitrogen purge for about 15 hours at 85°C. The mixture was subsequently cooled, filtered, washed repeatedly with deionized water, and dried overnight under vacuum at 70°. The dried material was designated Sample A.

[0088] Sample A was analyzed by conventional x-ray diffraction techniques which produced the trace presented in Fig. 1. The trace includes peaks characteristic of a hydrotalcite structure having a $d(001)$ value of 7.62 Angstrom units. Additionally, Sample A was analyzed for metals by inductively coupled plasma techniques and the metals were reported as 20.6 percent magnesium, 12.0 percent aluminum, 6.1 cerium, and 450 ppm sodium. The reported metals correspond to a hydrotalcite clay having the formula:

Example 2: Calcination of a Layered Mixed Hydroxide at 450°

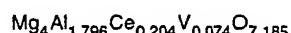
[0089] A portion of the dried material produced by the procedure described in Example 1 above was heated in air at a rate of about 20°C per minute until a temperature of 450°C was achieved. The material was held at 450° for 15 hours and then cooled. The material calcined at 450° was designated Sample B.

Example 3: Calcination of a Layered Mixed Hydroxide at 850°

[0090] A portion of the dried material produced by the procedure described in Example 1 above was heated in air at a rate of about 20°C per minute until a temperature of 850° was achieved. The material was held at 850° for 15 hours and then cooled. The material calcined at 850° was designated Sample C.

Example 4: Vanadation of 450° Calcined Material

[0091] A solution was prepared by blending 0.23 grams of NH_4VO_3 with 6.22 grams of deionized water. The proportions of the solution had been carefully chosen to provide a pH in the range of 6 to 8 in order to stabilize metavanadate ions (VO_3^{4-}). The solution was thoroughly mixed with 4.82 grams of Sample B which was described in Example 2 above. The resulting mixtures was dried under vacuum at 70°C overnight and then calcined at 450° to produce a vanadated material designated Sample D. Based on the proportions of reactants, it is estimated that the theoretical formula of Sample D is approximately:



[0092] Subsequent analyses of Sample D were reported as B.E.T. surface area of 192 m²/g, average pore radius of 81 Angstrom units, micropore area of 50 m²/g, and micropore volume of 0.023 cc/g.

Example 5: Vanadation of 850° Calcined Material

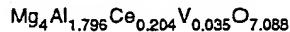
[0093] The procedure of Example 4 was performed again except that Sample C described in Example 3 above was vanadated and calcined. The resulting material was designated Sample E. The estimated theoretical formula for Sample E is identical to the formula presented above for Sample D.

[0094] Subsequent analyses indicated that Sample E had a B.E.T. surface area of 119 m²/g, an average pore radius of 91 Angstrom units, a micropore area of 6 m²/g, and a micropore volume of 0.003 cc/g. High resolution electron photomicrography of Sample D, supported by scanning electron microscope analyses, indicated that a significant fraction of the microcrystallites present were composed of a solid solution phase having aluminum oxide dispersed in a magnesium oxide crystal lattice.

Example 6: Reactant Limited Vanadation

[0095] A relatively dilute vanadate solution was prepared by blending 0.11 grams of NH_4VO_3 with 4.0 liters of deionized water. The proportions of the solution had been chosen to provide a pH in the range which stabilizes the metavanadate form of the anion. The dilute solution was thoroughly mixed with 4.82 grams of Sample B which was described in Example 2 above. The resulting mixture was filtered, then dried under vacuum at 70°C overnight and calcined at 450° to produce a partially vanadated material.

[0096] Based on the proportions of reactants, it is estimated that the theoretical formula of the partially vanadated material is approximately:

Example 7: Performance Testing of Sample D

[0097] A portion of Sample D which was described in Example 4 above was subjected to thermal gravimetric analysis during sequential periods of exposure to an oxidizing gas mixture including 5000 ppm sulfur dioxide, 2 percent oxygen and balance helium and to a reducing gas mixture including 50 percent hydrogen and balance helium. The temperature of the oxidizing gas was about 735°C, while the temperature of the reducing gas was about 640°C. Each exposure was preceded by a period of helium purge at the corresponding temperature.

[0098] The sample, which weighed 19.7363 milligrams at the outset, exhibited a relative weight increase of 84.6 percent during ninety minutes of exposure to the oxidizing gas mixture. An almost immediate relative weight decrease of 87.3 percent was observed on exposure to the reducing gas mixture. Figure 2 depicts the relationship of relative sample weight, expressed as a percentage of the weight at the outset, to elapsed time in minutes for one oxidizing and reducing cycle of the thermal gravimetric analysis for Sample D.

Example 8: Performance Testing of Sample E

[0099] The procedure of Example 7 above was repeated with a portion of Sample E which was described in Example 5 above. The sample weighed 20.8923 milligrams at the outset. The sample increased in relative weight by 83.3 percent while exposed to the oxidizing gas mixture, and decreased in relative weight by 84.1 percent weight during the exposure to the reducing gas, based on the weight at the outset. Figure 3 shows the relationship of relative sample weight, expressed as a percentage of the weight at the outset, to elapsed time in minutes for one oxidizing and reducing cycle of the thermal gravimetric analysis for Sample E.

[0100] Some of the Sample E material subjected to thermal gravimetric analysis was also tested for thermal gravimetric performance during a second oxidizing and reducing cycle and a third oxidizing and reducing cycle. The sample weight at the outset of the second cycle was 16.8988 milligrams, with the third cycle following immediately after the second. Relative sample weight as of a function of elapsed time as well as a temperature trace for the second and third cycles of Sample E is presented graphically in Fig. 4.

Example 9: Performance Testing of a Spinel Absorbent

[0101] A widely used sulfur oxide absorbent based on a spinel composition was commercially obtained and designated Sample F for the purpose of performing a control experiment. Sample F is not of the present invention. However, Sample F was subjected to one oxidizing and reducing cycle of the performance test described in Example 7 and Example 8 above. Sample F exhibited a 47.0 percent increase in relative weight over a period of 90 minutes exposure to the oxidizing gas containing sulfur dioxide. Exposure to the reducing gas containing hydrogen caused an almost immediate relative weight decrease of 50.3 percent.

[0102] The results of performance testing produced in Example 7, Example 8 and Example 9 are presented in Table I, below.

TABLE I

Absorbent Sample	Cycle	Relative Weight Increase (percent)	Time mins.	Relative Weight Decrease (percent)	Time mins.
D	1	84.6	90	87.3	rapid
E	1	83.3	90	84.1	rapid

TABLE I (continued)

Absorbent Sample	Cycle	Relative Weight Increase (percent)	Time mins.	Relative Weight Decrease (percent)	Time mins.
5 F	2	76.2	90	77.4	rapid
	3	78.3	90	not studied	
	1	47.0	90	50.3	rapid

10 [0103] Inspection of Table I reveals that the absorbents prepared according to the present invention, Sample D and Sample E, demonstrated a significantly larger capacity for sulfur dioxide absorption than did the control sample, Sample F. Additionally, Sample E of the present invention continued to absorb more sulfur dioxide on its second and third oxidizing cycles than did control Sample F on its initial oxidizing cycle. The results are especially surprising because Sample F is a commercially obtained absorbent which is representative of widely accepted and currently utilized absorbent technology.

15 [0104] For the purposes of the present specification, "predominantly" is defined as mostly or more often than not. In quantitative terms, predominantly denotes 50 percent or more. "Substantially" is defined as being present in significant proportions or having sufficient frequency so as to measurably affect macroscopic qualities of an associated compound or system. Where the amount required for such significant and measurable impact is not clear, substantially is synonymous with 20 percent or more. "Essentially" is defined as absolutely but allowing for some small variations which 20 have a negligible effect on macroscopic qualities and final outcome. Variations of about one percent can often exist without any detectable change in essential qualities.

25 **Claims**

1. A composition which includes microcrystallites collectively of the formula:



30 where M^{2+} is a divalent metal selected from the group consisting of magnesium, calcium, zinc, barium and strontium;

35 m is 1.1 to 3.5;

M^{3+} is a trivalent metal selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium, and cobalt;

p is 0.01 to 0.4;

T is vanadium, tungsten or molybdenum, with the proviso that T and M^{3+} cannot both be vanadium when M^{2+} is magnesium

40 r is 0.01 to 0.2; s is 2.5 when T is vanadium or 3 when T is tungsten or molybdenum;

45 wherein the microcrystallites are substantially composed of solid solution microcrystallites having aluminum oxide dispersed in a monoxide of the divalent metal and of spinel phase microcrystallites, each of the microcrystallites having a greatest linear dimension in the range of 0.1 to 30 nanometers.

2. The composition according to claim 1 wherein the microcrystallites are additionally composed of trivalent metal oxide phase microcrystallites.

50 3. The composition according to Claim 1 or Claim 2 wherein the spinel phase microcrystallites are essentially of the formula:



55 4. A process for manufacturing a composition according to any one of Claims 1 to 3 which includes:

blending water, about two molar parts of a salt of a divalent metal selected from the group consisting of mag-

nesium, calcium, zinc, strontium and barium, and about one molar part in sum of an aluminum salt and a salt of a trivalent metal selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium, and cobalt to produce a mixture;

5 heating the mixture to a temperature in the range of 50°C to 100°C for at least one hour;

recovering from the mixture an anionic layered mixed hydroxide having relatively small anions selected from the group consisting of CO_3 , OH , SO_3 , SO_4 , Cl and NO_3 ;

10 calcining the recovered layered mixed hydroxide for not less than one hour at a temperature in the range of 450°C to 1000°C, to produce a dehydrated material which is essentially devoid of the relatively small anions; mixing the dehydrated material with an aqueous solution including 0.01 to less than two molar parts of a metalate salt containing vanadate, tungstenate, or molybdate anions to produce a slurry, the solution also including an amount of an alkalinity control agent appropriate to stabilize the anions in monometalate, dimetalate, trimetalate or tetrametalate form; and

15 recovering solids from the slurry and calcining the solids to produce an at least partially collapsed composition suitable for use as a sulfur oxide absorbent.

15 5. The process according to Claim 4 wherein the metalate salt is blended in an amount sufficient to produce a concentration of the anion in the liquid portion of the slurry which is in the range of about 0.01 to 1 molar and wherein the anion is a vanadate.

20 6. The process according to Claim 4 or Claim 5 wherein the divalent metal is magnesium and the trivalent metal is cerium.

7. The process according to any one of Claims 4 to 6 wherein the microcrystallites are additionally composed of trivalent metal oxide phase microcrystallites.

25 8. A process for manufacturing a composition according to any one of Claims 1 to 3 which includes:

30 blending water, about two molar parts of a salt of a divalent metal selected from the group consisting of magnesium, calcium, zinc, strontium and barium, about one molar part in sum of an aluminum salt and a salt of a trivalent metal selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium, and cobalt, 0.01 to less than two molar parts of a metalate salt containing vanadate, tungstenate, or molybdate anions, and an amount of an alkalinity control agent appropriate to stabilize the anions in monometalate, dimetalate, trimetalate or tetrametalate form to produce a mixture;

35 heating the mixture to a temperature in the range of 50° to 100°C for at least one hour;

recovering from the mixture an anionic layered mixed hydroxide; and

calcining the recovered layered mixed hydroxide for not less than one hour at a temperature in the range of 450°C to 1000°C, to produce an at least partially collapsed composition suitable for use as a sulfur oxide absorbent.

40 9. The process according to Claim 8 wherein the recovered layered mixed hydroxide is of the formula:

$$\text{M}^{2+}_{2m} \text{Al}_{(2-p)} \text{M}^{3+}_p (\text{OH})_{(4m+4)} \text{J}^v_{(kv)} \text{A}^q_{(2-kq)} \cdot x\text{H}_2\text{O}$$

45 where M^{2+} is a divalent metal selected from the group consisting of magnesium, calcium, zinc, barium, and strontium;

50 m is 1.1 to 3.5;
 M^{3+} is a trivalent metal selected from the group consisting of cerium, lanthanum, iron, chromium, vanadium, and cobalt;
 p is 0.01 to 0.4;

55 J is VO_3 , HVO_4 , VO_4 , V_2O_7 , HV_2O_7 , V_3O_9 , V_4O_{12} , WO_4 , or MoO_4 ;
 v is the net ionic charge associated with J ;
 k is 0.01 to less than 2;
 A is CO_3 , OH , SO_3 , SO_4 , Cl , or NO_3 ;
 q is the net ionic charge associated with A ; and;
 x is a positive number.

10. The process according to Claim 9 wherein the microcrystallites are additionally composed of trivalent metal oxide phase microcrystallites.

11. The process according to Claim 9 or Claim 10 wherein the monoxide is magnesium oxide.

5

12. The process according to any one of Claims of Claim 9 to Claim 11 wherein A is carbonate.

13. A process for separating sulfur oxides from a gaseous mixture containing sulfur oxides, which includes absorbing sulfur oxides by exposing a gaseous mixture containing sulfur oxides with dehydrated and at least partially collapsed composition according to any one of Claims 1 to 3

10

14. The process according to Claim 13 which further includes desorbing the sulfur oxides by contacting the dehydrated and at least partially collapsed composition with a hydrocarbon in the presence of a cracking catalyst.

15

15. The process according to Claim 13 or Claim 14 which further includes exposing a layered mixed hydroxide to the gaseous mixture containing sulfur oxides at a temperature in the range of 450°C to 1000°C to produce the dehydrated and at least partially collapsed composition.

20

16. The process according to any one of Claims 13 to 15 wherein the desorbing produces sulfur compounds which include hydrogen sulfide.

17. A process for the cyclic, fluidized catalytic-cracking of a hydrocarbon feedstock containing organic sulfur compounds wherein:

25

(i) the feedstock is mixed with a particulate cracking catalyst in a reaction zone at a temperature in the range of 430°C to 730°C to produce cracked hydrocarbons and a coke containing sulfur, relatively volatile components, and relatively less volatile components;

(ii) the cracking catalyst is separated from the cracked hydrocarbons and passed to a stripping zone where the catalyst is exposed to a stripping gas stream at a temperature in the range of 430°C to 730°C to substantially elutriate the volatile components from the cracking catalyst;

(iii) the cracking catalyst is passed to a catalyst regeneration zone where sulfur and the relatively less volatile components are substantially eradicated from the cracking catalysts by burning in the presence of an oxidizing gas at a temperature in the range of 565°C to 790°C to produce an effluent gas stream including carbon oxides and sulfur oxides; and

(iv) the cracking catalyst is returned to the reaction zone;

30

wherein the total amount of sulfur oxides in the effluent gas stream of the regeneration zone are reduced by the method which includes absorbing at least a portion of the sulfur oxides in the regeneration zone with a fluidizable particulate solid which includes a dehydrated and at least partially collapsed composition according to any one of Claims 1 to 3.

40

18. The process according to Claim 17 which further includes removing the absorbed sulfur oxides from the particulate solid by exposing the particulate solid to the hydrocarbon feedstocks in the reaction zone.

45

19. The process according to Claim 17 or Claim 18 which further includes contacting an anionic layered mixed hydroxide composition with the oxidizing gas in the regeneration zone to produce the dehydrated and at least partially collapsed composition.

50

Patentansprüche

1. Eine Zusammensetzung, die Mikrokristallite der folgenden zusammenfassenden Formel umfaßt:



55

in der M^{2+} ein zweiwertiges Metall aus der Gruppe: Magnesium, Kalzium, Zink, Barium und Strontium;

5 m 1,1 bis 3,5;
M³⁺ ein dreiwertiges Metall aus der Gruppe: Cer, Lanthan, Eisen, Chrom, Vanadin und Kobalt;
p 0,01 bis 0,4;
T Vanadium, Wolfram oder Molybdän unter der Bedingung, daß T und M³⁺ nicht beide Vanadium sein können,
wenn M²⁺ Magnesium ist;
r 0,01 bis 0,2 und s 2,5, wenn T Vanadium ist, oder 3, wenn T Wolfram oder Molybdän ist, bedeuten,
wobei die Mikrokristallite im wesentlichen aus Mikrokristalliten von festen Lösungen zusammengesetzt sind, die
10 Aluminiumoxid in einem Monoxid des zweiwertigen Metalls dispergiert enthalten, und aus Mikrokristalliten der
Spinelphase zusammengesetzt sind, wobei jeder Mikrokristallit eine größte lineare Ausdehnung im Bereich von
0,1 bis 30 nm besitzt.

15 2. Die Zusammensetzung nach Anspruch 1, wobei die Mikrokristallite zusätzlich aus Mikrokristalliten mit dreiwertigem
Metalloxid-Phase zusammengesetzt sind.

20 3. Die Zusammensetzung nach Anspruch 1 oder 2, wobei die Mikrokristallite der Spinelphase im wesentlichen die
folgende Formel besitzen:

25
$$\text{MgAl}_2\text{O}_4$$

30 4. Verfahren zur Herstellung einer Zusammensetzung nach einem der Ansprüche 1 bis 3, umfassend:
man mischt Wasser, etwa zwei molare Teile eines Salzes eines zweiwertigen Metalls aus der Gruppe: Ma-
gnesium, Kalzium, Zink, Strontium und Barium und insgesamt etwa einen molaren Teil eines Aluminiumsalzes
35 und eines Salzes eines zweiwertigen Metalls aus der Gruppe: Cer, Lanthan, Eisen, Chrom, Vanadium und
Kobalt zur Herstellung eines Gemisches;
man erhitzt das Gemisch auf eine Temperatur im Bereich von 50°C bis 100°C wenigstens eine Stunde lang;
man gewinnt aus dem Gemisch ein anionisches geschichtete gemischtes Hydroxid mit relativ kleinen Anionen
40 aus der Gruppe: CO₃, OH, SO₃, SO₄, Cl und NO₃;
man kalziniert das gewonnene geschichtete gemischte Hydroxid wenigstens eine Stunde lang bei einer Tem-
peratur im Bereich von 450°C bis 1000°C zur Erzeugung eines dehydratisierten Materials, das im wesentlichen
45 ohne relativ kleine Anionen ist;
man mischt das dehydratisierte Material mit einer wäßrigen Lösung, die 0,01 bis weniger als 2 molare Teile
eines Metallat-Salzes, das Vanadat-, Wolframat- oder MolybdatAnionen enthält, zur Erzeugung einer Auf-
schämmung, wobei die Lösung auch eine Menge eines die Basizität steuernden Mittels enthält, die geeignet
50 ist, die Anionen in Monometallat-, Dimetallat-, Trimetallat- oder Tetrametallat-Form zu stabilisieren; und
man gewinnt Feststoffteilchen aus der Aufschämmung und kalziniert die Feststoffteilchen zur Erzeugung von
einer wenigstens teilweise zusammengesunkenen Zusammensetzung, die zur Verwendung als ein Schwei-
floxid-Absorptionsmittel geeignet ist.

55 5. Verfahren nach Anspruch 4, wobei das Metallatsalz in einer genügenden Menge gemischt wird um eine Konzen-
tration des Anions in dem flüssigen Anteil der Aufschämmung zu erzeugen, der im Bereich von etwa 0,01 bis 1
molar liegt und worin das Anion ein Vanadat ist.

60 6. Verfahren nach Anspruch 4 oder 5, wobei das zweiwertige Metall Magnesium und das dreiwertige Metall Cer ist.

65 7. Verfahren nach einem der Ansprüche 4 bis 6, wobei die Mikrokristallite zusätzlich aus Mikrokristalliten einer Oxid-
phase eines dreiwertigen Metalles zusammengesetzt sind.

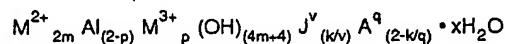
70 8. Verfahren zur Herstellung einer Zusammensetzung nach einem der Ansprüche 1 bis 3, umfassend:
man mischt Wasser, etwa 2 molare Teile eines Salzes eines zweiwertigen Metalls aus der Gruppe: Magnesium,
75 Kalzium, Zink, Strontium und Barium, etwa insgesamt 1 molares Teil eines Aluminiumsalzes und eines Salzes
eines dreiwertigen Metalls aus der Gruppe: Cer, Lanthan, Eisen, Chrom, Vanadium und Kobalt, 0,01 bis we-
niger als 2 molare Teile eines Metallatsalzes, das Vanadat-, Wolframat- oder Molybdatanionen enthält und eine
80 Menge eines die Basizität steuernden Mittels, die geeignet ist, die Anionen in Monometallat-, Dimetallat-,
Trimetallat- oder Tetrametallat-Form zu stabilisieren, zur Erzeugung eines Gemisches;

man erhitzt das Gemisch auf eine Temperatur im Bereich von 50°C bis 100°C während wenigstens einer Stunde;

man gewinnt aus dem Gemisch ein anionisches geschichtetes Hydroxid; und

man kalziniert das gewonnene geschichtete gemischte Hydroxid während nicht weniger als einer Stunde bei einer Temperatur im Bereich von 450°C bis 1000°C zur Erzeugung einer wenigstens teilweise zusammengesunkenen Zusammensetzung für den Gebrauch als Schwefeloxid-Absorptionsmittel.

9. Verfahren nach Anspruch 8, wobei das gewonnene geschichtete gemischte Hydroxid die folgende Formel besitzt:



in der M^{2+} ein zweiwertiges Metall aus der Gruppe: Magnesium, Kalzium, Zink, Barium und Strontium;

15 m 1,1 bis 3,5;

M^{3+} ein dreiwertiges Metall aus der Gruppe: Cer, Lanthan, Eisen, Chrom, Vanadium und Kobalt;

p 0,01 bis 0,4;

J VO_3 , HVO_4 , VO_4 , V_2O_7 , HV_2O_7 , V_3O_9 , V_4O_{12} , WO_4 oder MoO_4 ;

v die Ionen-Nettoladung von J;

20 k 0,01 bis weniger als 2;

A CO_3 , OH , SO_3 , SO_4 , Cl , oder NO_3 ;

q die Ionen-Nettoladung von A; und;

x eine positive Zahl bedeuten.

25 10. Verfahren nach Anspruch 9, wobei die Mikrokristallite zusätzlich aus Mikrokristalliten der Oxidphase von dreiwertigem Metall zusammengesetzt sind.

11. Verfahren nach Anspruch 9 oder 10, wobei das Monoxid Magnesiumoxid ist.

30 12. Verfahren nach einem der Ansprüche 9 bis 11, wobei A Karbonat ist.

13. Verfahren zur Abtrennung von Schwefeloxiden aus einem Schwefeloxide enthaltenden Gasgemisch, umfassend die Absorption von Schwefeloxiden durch Aussetzen eines schwefeloxidhaltigen Gasgemisches einer dehydratisierten und wenigstens teilweise zusammengesunkenen Zusammensetzung nach einem der Ansprüche 1 bis 3.

35 14. Verfahren nach Anspruch 13, ferner umfassend die Desorption der Schwefeloxide durch Inkontaktbringen der dehydratisierten und wenigstens teilweise zusammengesunkenen Zusammensetzung mit einem Kohlenwasserstoff in Gegenwart eines Crackkatalysators.

40 15. Verfahren nach Anspruch 13 oder 14, umfassend ferner das Aussetzen eines geschichteten gemischten Hydroxids der Schwefeloxide enthaltenden Gasmischung bei einer Temperatur im Bereich von 450°C bis 1000°C zur Erzeugung der dehydratisierten und wenigstens teilweise zusammengesunkenen Zusammensetzung.

45 16. Verfahren nach einem der Ansprüche 13 bis 15, wobei das Desorbieren Schwefelverbindungen erzeugt, die Schwefelwasserstoff einschließen.

17. Verfahren zum zyklischen fluidisierten katalytischen Cracken eines Kohlenwasserstoff-Einsatzmaterials, das organische Schwefelverbindungen enthält, wobei:

50 (i) das Einsatzmaterial mit einem teilchenförmigen Crackkatalysator in einer Reaktionszone bei einer Temperatur im Bereich von 430°C bis 730°C gemischt wird zur Erzeugung von gecrackten Kohlenwasserstoffen und einem Koksrückstand, der Schwefel, relativ flüchtige Komponenten und relativ weniger flüchtige Komponenten enthält;

(ii) der Crackkatalysator von den gecrackten Kohlenwasserstoffen getrennt und in eine Stripzone übergeleitet wird, wo der Katalysator einem Stripgas bei einer Temperatur im Bereich von 430°C bis 730°C ausgesetzt wird, um im wesentlichen die flüchtigen Komponenten aus dem Crackkatalysator auszuwaschen.

(iii) der Crackkatalysator in eine Katalysator-Regenerierungszone geleitet wird, wo Schwefel und die relativ weniger flüchtigen Komponenten im wesentlichen aus den Crackkatalysatoren durch Verbrennen in Anwe-

senheit eines oxidierenden Gases bei einer Temperatur im Bereich von 565°C bis 790°C entfernt werden zur Erzeugung eines Abgasstroms, der Kohlenoxide und Schwefeloxide enthält; und
 (iv) der Crackkatalysator in die Reaktionszone zurückgeführt wird;

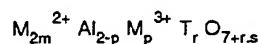
5 wobei die Gesamtmenge an Schwefeloxiden in dem Abgasstrom der Reaktionszone durch das Verfahren reduziert wird, das das Absorbieren wenigstens eines Teils der Schwefeloxide in der Reaktionszone mit einem fluidisierbaren teilchenförmigen Festkörper umfaßt, welcher eine dehydratisierte und wenigstens teilweise zusammengesunkene Zusammensetzung nach einem der Ansprüche 1 bis 3 umfaßt.

10 18. Verfahren nach Anspruch 17, das ferner die Entfernung der absorbierten Schwefeloxide aus dem teilchenförmigen Festkörper umfaßt, indem man den teilchenförmigen Festkörper den Kohlenwasserstoff-Einsatzmaterialien in der Reaktionszone aussetzt.

15 19. Verfahren nach Anspruch 17 oder 18, das ferner das Inkontaktbringen einer anionischen geschichteten Zusammensetzung aus gemischten Hydroxiden mit dem oxidierenden Gas in der Reaktionszone umfaßt, wobei die dehydratisierte und wenigstens teilweise zusammengesunkene Zusammensetzung erzeugt wird.

Revendications

20 1. Composition qui comprend des microcristallites ayant globalement la formule :



25 dans laquelle

- M^{2+} est un métal divalent choisi au sein du groupe comprenant le magnésium, le calcium, le zinc, le baryum et le strontium ;
- m varie entre 1,1 et 3,5 ;
- M^{3+} est un métal trivalent choisi au sein du groupe comprenant le cérium, le lanthane, le fer, le chrome, le vanadium et le cobalt ;
- p varie de 0,01 à 0,4 ;
- T représente le vanadium, le tungstène ou le molybdène, à la condition que T et M^{3+} ne représentent pas tous deux le vanadium lorsque M^{2+} est le magnésium ;
- r varie de 0,01 à 0,2 ; s est égal à 2,5 lorsque T représente le vanadium ou est égal à 3 lorsque T représente le tungstène ou le molybdène ; composition dans laquelle les microcristallites sont substantiellement composés de microcristallites sous forme de solutions solides ayant de l'oxyde d'aluminium dispersé dans un monoxyde du métal divalent, et de microcristallites en phase spinelle, chacun des microcristallites ayant sa plus grande dimension linéaire comprise entre 0,1 et 30 nanomètres.

30

35

40

2. Composition selon la revendication 1, dans laquelle les microcristallites sont en outre composés de microcristallites de phase oxyde de métal trivalent.

45 3. Composition selon la revendication 1 ou la revendication 2, dans laquelle les microcristallites de phase spinelle sont essentiellement de formule :



50 4. Procédé de fabrication d'une composition selon l'une quelconque des revendications 1 à 3 qui comprend :

- l'opération de mélange à l'eau, d'environ deux parties molaires d'un sel d'un métal divalent choisi au sein du groupe comprenant le magnésium, le calcium, le zinc, le strontium et le baryum, et d'environ une partie molaire au total d'un sel d'aluminium et d'un sel d'un métal trivalent choisi au sein du groupe comprenant le cérium, le lanthane, le fer, le chrome, le vanadium et le cobalt, pour donner un mélange ;
- le chauffage dudit mélange à une température comprise entre 50°C et 100°C pendant au moins une heure ;
- la récupération à partir du mélange, d'un hydroxyde mixte à couche anionique ayant des anions relativement

EP 0 762 930 B1

petits choisis au sein du groupe comprenant CO_3 , OH , SO_3 , SO_4 , Cl et NO_3 ,

- la calcination de l'hydroxyde mixte à couche anionique ainsi récupéré, pendant au moins une heure à une température comprise entre 450°C et 1000°C , pour donner un matériau déshydraté qui est essentiellement dépourvu des anions relativement petits ;
- l'opération de mélange du matériau déshydraté avec une solution aqueuse contenant 0,01 à moins de deux parties molaires d'un sel métallate contenant des anions vanadate, tungstate et molybdate pour donner une suspension, la solution contenant aussi une quantité d'agent de contrôle de l'alcalinité, appropriée à la stabilisation des anions dans la forme monométallate, dimétallate, trimétallate ou tétramétallate ; et
- la récupération des solides à partir de la suspension, et la calcination desdits solides pour donner une composition au moins partiellement dégradée, appropriée à l'emploi en tant qu'absorbant des oxydes de soufre.

5. Procédé selon la revendication 4, dans lequel le sel métallate est mélange avec une quantité suffisante pour produire dans la portion liquide de la suspension, une concentration molaire de l'anion qui soit comprise entre environ 0,01 à 1, et dans lequel l'anion est un vanadate.

15. Procédé selon la revendication 4 ou la revendication 5, dans lequel le métal divalent est le magnésium et le métal trivalent est le cérium.

20. Procédé selon l'une quelconque des revendications 4 à 6, dans lequel les microcristallites sont en outre composés de microcristallites de phase oxyde de métal trivalent.

25. Procédé de fabrication d'une composition selon l'une quelconque des revendications 1 à 3 qui comprend :

- l'opération de mélange à l'eau, d'environ deux parties molaires d'un sel d'un métal divalent choisi au sein du groupe comprenant le magnésium, le calcium, le zinc, le strontium et le baryum, d'environ une partie molaire au total d'un sel d'aluminium et d'un sel d'un métal trivalent choisi au sein du groupe comprenant le cérium, le lanthane, le fer, le chrome, le vanadium et le cobalt, d'environ 0,01 à moins de deux parties molaires d'un sel métallate contenant des anions vanadate, tungstate ou molybdate, et d'une quantité d'un agent de contrôle de l'alcalinité appropriée à la stabilisation des anions dans la forme monométallate, dimétallate, trimétallate ou tétramétallate, pour donner un mélange ;
- le chauffage dudit mélange à une température comprise entre 50°C et 100°C pendant au moins une heure ;
- la récupération à partir du mélange, d'un hydroxyde mixte à couche anionique ; et
- la calcination de l'hydroxyde mixte à couche anionique ainsi récupéré, pendant au moins une heure à une température comprise entre 450°C et 1000°C , pour donner une composition au moins partiellement dégradée, appropriée à l'emploi en tant qu'absorbant des oxydes de soufre.

35. Procédé selon la revendication 8, dans lequel l'hydroxyde mixte à couche anionique ainsi récupéré est de formule :

40.
$$\text{M}_{2m}^{2+} \text{Al}_{(2-p)} \text{M}_p^{3+} (\text{OH})_{(4m+4)} \text{J}_{(k/v)}^v \text{A}_{(2-k/q)}^q \cdot x\text{H}_2\text{O}$$

dans laquelle

- M^{2+} est un métal divalent choisi au sein du groupe comprenant le magnésium, le calcium, le zinc, le baryum et le strontium ;
- m varie de 1,1 à 3,5 ;
- M^{3+} est un métal trivalent choisi au sein du groupe comprenant le cérium, le lanthane, le fer, le chrome, le vanadium et le cobalt ;
- p varie de 0,01 à 0,4 ;
- J représente VO_3 , HVO_4 , VO_4 , V_2O_7 , HV_2O_7 , V_3O_9 , V_4O_{12} , WO_4 ou MoO_4 ;
- v est la charge ionique nette associée à J ;
- k varie de 0,01 à moins de 2 ;
- A représente CO_3 , OH , SO_3 , Cl ou NO_3 ;
- q est la charge ionique nette associée à A ; et
- x est un nombre positif.

45. Procédé selon la revendication 9, dans lequel les microcristallites sont composés en outre de microcristallites de phase oxyde de métal trivalent.

50. Procédé selon la revendication 9, dans lequel les microcristallites sont composés en outre de microcristallites de phase oxyde de métal trivalent.

55. Procédé selon la revendication 9, dans lequel les microcristallites sont composés en outre de microcristallites de phase oxyde de métal trivalent.

11. Procédé selon la revendication 9 ou la revendication 10 dans lequel le monoxyde est l'oxyde de magnésium.
12. Procédé selon l'une quelconque des revendications 9 à 11, dans lequel A représente un carbonate.
- 5 13. Procédé de séparation d'oxydes de soufre à partir d'un mélange gazeux contenant des oxydes de soufre, qui comprend l'absorption desdits oxydes de soufre par l'exposition d'un mélange gazeux contenant des oxydes de soufre à une composition déshydratée et au moins partiellement dégradée selon l'une quelconque des revendications 1 à 3.
- 10 14. Procédé selon la revendication 13, qui comprend aussi la désorption des oxydes de soufre par la mise en contact de la composition déshydratée et au moins partiellement dégradée, avec un hydrocarbure en présence d'un catalyseur de craquage.
- 15 15. Procédé selon la revendication 13 ou la revendication 14 qui comprend aussi l'exposition d'un hydroxyde mixte à couche, au mélange gazeux contenant des oxydes de soufre, à une température comprise entre 450°C et 1000°C pour donner la composition déshydratée et au moins partiellement dégradée.
- 20 16. Procédé selon l'une quelconque des revendications 13 à 15, dans lequel la désorption produit des composés soufrés qui comprennent le sulfure d'hydrogène.
17. Procédé pour le craquage catalytique fluidisé cyclique d'un produit de départ hydrocarbure contenant des composés organiques soufrés, dans lequel :
 - 25 (i) le produit de départ est mélangé avec un catalyseur particulaire de craquage dans une zone réactionnelle à une température comprise entre 430°C et 730°C pour donner des hydrocarbures craqués et un coke contenant du soufre, des composants relativement volatils et des composants relativement moins volatils ;
 - (ii) le catalyseur de craquage est séparé des hydrocarbures craqués et passé dans une zone d'extraction où le catalyseur est exposé à un courant gazeux d'extraction à une température comprise entre 430°C et 730°C dans le but d'extraire substantiellement les composants volatils du catalyseur de craquage ;
 - 30 (iii) le catalyseur de craquage est passé dans une zone de régénération où le soufre et les composants relativement moins volatils sont substantiellement extirpés desdits catalyseurs de craquage par combustion en présence d'un gaz oxydant, à une température comprise entre 565°C et 790°C pour donner un courant gazeux effluent contenant des oxydes de carbone et des oxydes de soufre ; et
 - (iv) le catalyseur de craquage est renvoyé vers la zone réactionnelle ;
- 35 dans lequel la quantité totale d'oxydes de soufre dans le courant gazeux effluent de la zone de régénération est réduite par la technique qui comprend l'absorption d'au moins une portion des oxydes de soufre dans la zone de régénération avec un solide particulaire fluidisable qui comprend une composition déshydratée et au moins partiellement dégradée selon l'une quelconque des revendications 1 à 3.
- 40 18. Procédé selon la revendication 17, qui comprend aussi l'élimination des oxydes de soufre absorbés à partir du solide particulaire, par exposition dudit solide particulaire aux produits de départ hydrocarbures dans la zone réactionnelle.
- 45 19. Procédé selon la revendication 17, qui comprend aussi la mise en contact d'une composition d'hydroxyde mixte à couche anionique avec le gaz oxydant dans la zone de régénération pour donner la composition déshydratée et au moins partiellement dégradée.

50

55

Fig. 1

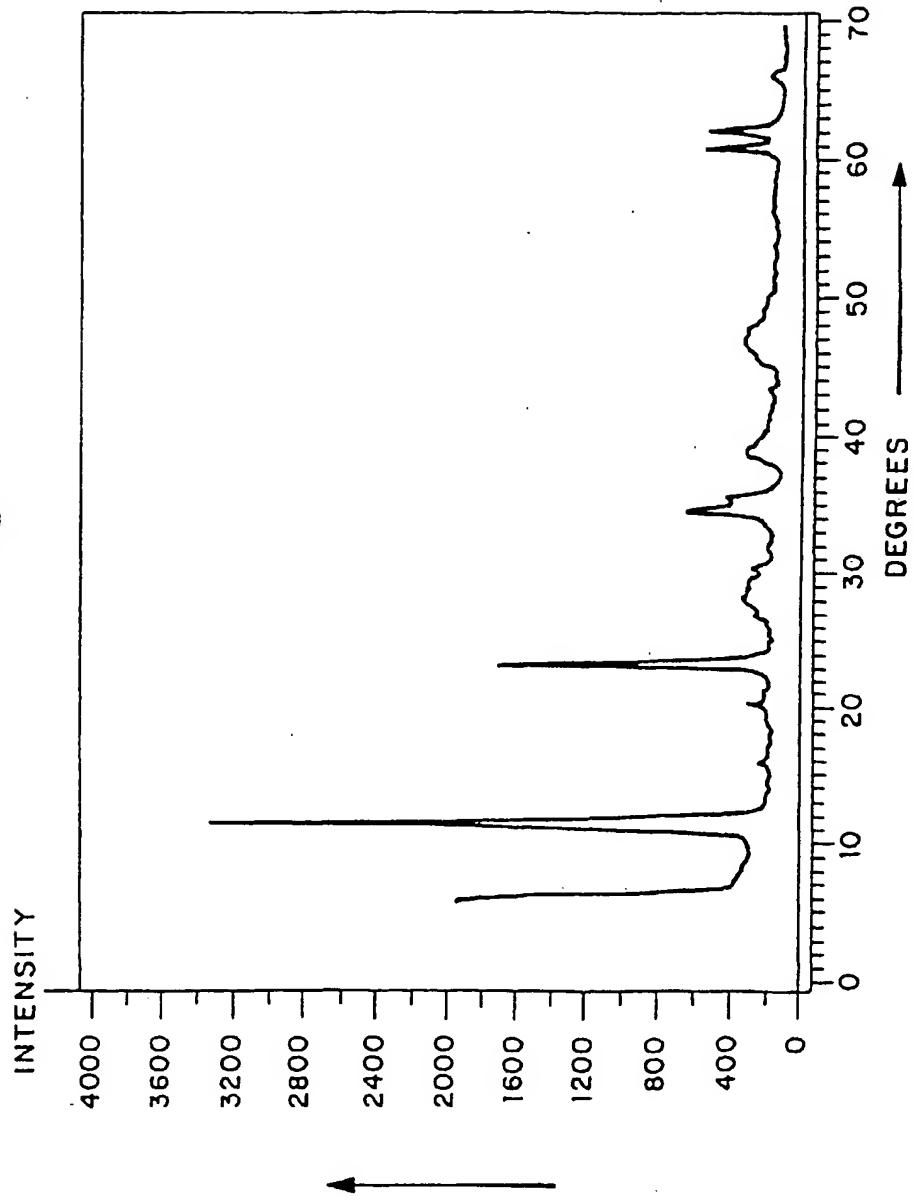


Fig. 2

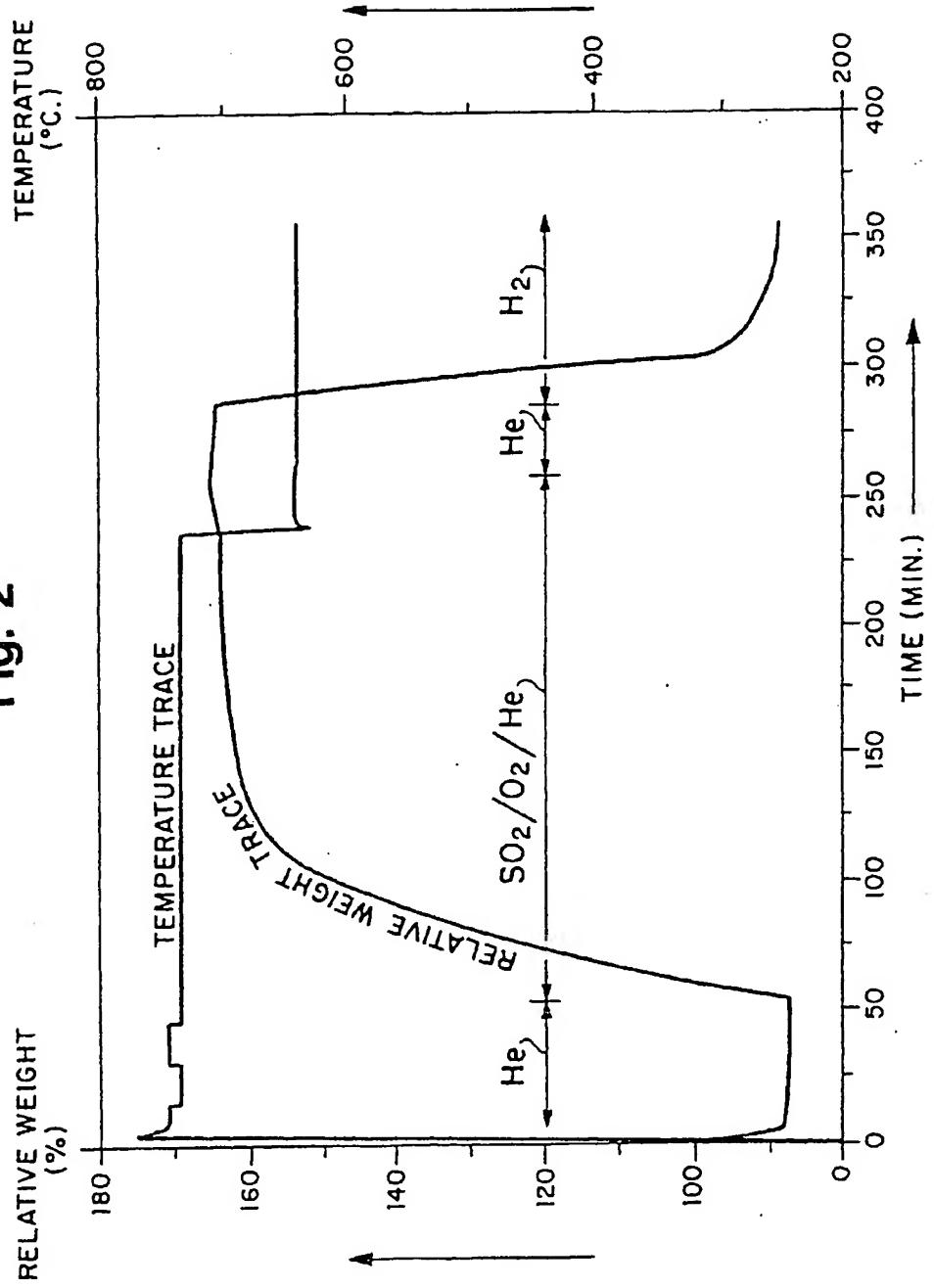


Fig. 3

